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Development of Environment Friendly Mimosa Tannin-Cornstarch Based Wood Adhesive

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Abstract**—**At present, formaldehyde-based adhesives such as urea formaldehyde (UF), melamine formaldehyde (MF), melamine-urea formaldehyde (MUF) etc. are mostly used in wood-based panel industry because of their high reactivity, chemical versatility and economic competitiveness. However, formaldehyde-based wood adhesives are produced from non-renewable resources. Hence, there has been a growing interest in the development of environment friendly, economically competitive, bio-based wood adhesives in order to meet wood-based panel industry requirements. In this study, as formaldehyde free adhesive, tannin and starch-based wood adhesive was synthesized. Citric acid and tartaric acid were used as hardener for the resin system. Solid content, viscosity and gel time analyzes of the prepared adhesive were performed in order to evaluate the adhesive processability. FTIR characterization technique was used to elucidate chemical structures of the cured adhesive samples. In order to evaluate the performance of the prepared bio-based resin formulation, particleboards were produced in laboratory scale and mechanical, physical properties of the boards were investigated. Besides, formaldehyde contents of the boards were determined by using perforator method. The obtained results revealed that the developed bio-based wood adhesive formulation can be a good potential candidate to use in wood-based panel industry with some developments.

Keywords**—**Wood adhesive, cornstarch, mimosa tannin, particleboard.

I. Introduction

THE wood-based panel industry produces wood-based composites such as particleboard and fiberboard, which are frequently used in our daily lives. Since formaldehyde-based resins have high chemical reactivity and low cost, they are frequently used as a binder in the production of these products [1], [2].

Formaldehyde-based resins are produced from fossil resources. In addition, formaldehyde content limits in boards are becoming more restrictive day by day. Therefore, bio-based resin synthesis studies have become significantly important [1], [3], [4].

When the literature studies were examined, it was seen that especially starch and tannin-based resin studies came to the fore. In the studies, it was stated that the most important problem of these resins is their lower chemical reactivity compared to formaldehyde-based resins [1], [5], [6].

One of the most effective methods used to improve the reactivity of resins is to increase the resin crosslink density [1], [7]. It has been stated that furanic derivatives are used as crosslinkers in starch and tannin-based resins and can also produce these furanic derivatives by caramelization of sugar at high temperatures [1], [8]. However, high pressing temperatures and long pressing times were required for board formation in these studies. One of the methods used to optimize the high press parameters was to catalyze the decomposition reaction of sugar. For this, acidic pH environments have been created.

In this study, a bio-based resin formulation was developed for particleboard production suitable for interior applications. Laboratory-scale particleboards were produced to determine the resin performance. Mechanical and physical tests of the produced boards were carried out. In addition, formaldehyde content values were determined. The obtained results showed that the synthesized Mimosa tannin (MT) and cornstarch (CS) based wood adhesive formulations were promising.

II. Materials and Methods

A. Chemicals and Reagents

Unmodified commercial grade CS was purchased from Sunar Mısır (Adana, Turkey); the moisture content was 11.9%. Commercial flavonoid Wattle bark (Mimosa) tannin (MT) was provided from Bondtite Pty. Ltd (Dorpspruit, South Africa); the moisture content was 7%. The CA and TA were supplied by Alfasol (Istanbul, Turkey). Laboratory scale particleboard production and board tests have been carried out in Kastamonu Entegre Ağaç San. Tic. A.Ş. [1].

B. Synthesis of CS-MT-S-CA and CS-MT-S-TA Adhesive

Primarily for resin synthesis with 55%, solid content by weight, 700 g of MT were added into 3215 g of distilled water and dispersed at room temperature under a mechanical stirrer. Then, 2140 g of sugar and 1145 g of CS were added to the tannin-water dispersion and mixed under a mechanical stirrer at room temperature until the starch was homogeneously dispersed. Finally, CA and TA were added to the resin system as a hardener. The hardener content used was 25% by weight of the resin solid content.

C. Physical Properties: Solid Content, Viscosity, and pH Measurements

In order to measure the solid content of the adhesive samples, firstly, a piece of aluminum foil was weighed and then the adhesive sample of about 1.5 g was added onto the weighed aluminum foil. Secondly, the adhesive samples were dried at 120 °C in an oven for 2 hours. Finally, the sample was removed from the oven and reweighed. The solid content (S) of the

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adhesives was determined from:

$$S = \frac{M_2 - M_0}{M_1 - M_0} x\ 100\%$$

where S, M_0, M_1, M_2 symbolized solid content; the mass of aluminum foil; the mass of aluminum foil and adhesive sample; the mass of aluminum foil and dry adhesive sample, respectively. Each solid content value was recorded from the average of three samples [1], [10].

The viscosity of the adhesive samples was measured at 20 °C and 200 rpm by using Brookfield CAP 2000+ viscometer, and each value was noted from the average of three tests. The pH value of the adhesive was also determined at 20 °C by using the Mettler Toledo pH meter.

D. Curing Time

25 wt. % TA and CA were added to the resin according to the resin solid content to determine the gelation time of the synthesized resin. After the added polycarboxylic acids were completely dissolved in the resin, approximately 3 grams of sample were taken and placed in a glass test tube. As soon as the glass test tube is dipped into the boiling water with a stirring rod, the rod is started to be mixed and the stopwatch is started. Mixing continued until the resin was completely cured. The point at which the rod could no longer be lifted from the resin was recorded as the resin gel time by pausing the time [10].

E. Fourier Transform Infrared (FT-IR) Spectroscopy

The chemical structure of MT, CS, CA, and the cured adhesive sample was elucidated by using FT-IR, Bruker Tensor 37 equipment. Each sample was scanned between 4000–400 cm^{-1}.

F. Particleboard Preparation and Testing

Three-layer laboratory-scale particleboards of dimension 500 mm x 500 mm x 12 mm were prepared. Three-layer particleboards were composed of two surface layers and one core layer. The total resin solid was 15% by weight for the surface layers and 10% for the core layer. Particleboards bonded with the CS-MT-S-CA and CS-MT-S-TA adhesive have been assembled and hot-pressed at 210 °C for 3,2 minutes press time. Particles were dried to approximately 4% moisture content prior to application of resin. Aimed board density was 700 g/cm^3. All tests were conducted in accordance with appropriate European Standards. Internal bond (IB), bending strength (BS), modulus of elasticity (MOE), and surface soundness of the produced particleboards were performed according to EN 319, EN 310, EN 311 test standards, respectively.

G. Formaldehyde Content by Perforator Method

Formaldehyde content of the produced boards was measured in accordance with the European Norm (EN 12460-5) by using the perforator method.

III. Results and Discussion

A. Physical Properties: Solid Content, Viscosity, and pH Measurements

The solid content of the resin was 54,59%, viscosity value was 90 mPa-s and pH value was 1,25. The resulting resin solids content was such that it would not generate excessive moisture in the hot pressing process. In addition, the resin viscosity value was sufficient to distribute the resin homogeneously on the chips [1], [10]. The resin pH value is at such a level that it catalyzes the thermal decomposition of sugar and creates more furanic derivatives that act as crosslinkers in the resin system per unit time [1], [9].

B. Curing Time

Curing time is one of the most important indicators of resin reactivity. Resin reactivity is critical for the wood-based panel industry as it directly affects the amount of resin usage and press parameters in the board production process. It has been observed that the curing time (about 60 sec.) of the synthesized resin formulations is at a good level when compared to the biobased resins developed in previous studies [10]. Thus, it can be said that the developed bio-based resin formulation is a potential candidate for the wood-based panel industry.

C. Fourier Transform Infrared (FT-IR) Spectroscopy

The chemical structures of the CS, MT, CA, and the cured adhesive sample were characterized with FT-IR and their spectra were shown in Fig. 1. As could be seen from Fig. 1, compared with the CS spectrum, the broad band at around 3300–3400 cm^{-1} related to the hydroxyl groups of the starch gradually weakened in the cured resin spectrum [11].

Besides, a new peak at 1715 cm^{-1} which was ascribed to the –CO = —carbonyl group which could be derived from the carboxyl group and/or ester group was detected in the FT-IR spectrum of the cured resin [12]. These observations suggested that an esterification reaction occurred between the hydroxyl groups of CS and carboxylic acid groups of CA (Fig. 2) [13]. On the other hand, the detected bands at 1587 and 1458 cm^{-1} in the MT spectrum which were attributed to the aromatic –CC = —stretching, were disappeared in the cured resin spectrum possibly due to the increment of the aromatic ring substitution of tannin [14]. The chemical structure of the MT was shown in Fig. 2 [15]. Besides, the new peaks at 1517 and 772 cm^{-1} were detected according to the FT-IR spectrum of the cured resin, which were respectively ascribed to the characteristic –CC = – –stretching vibration and unsubstituted CH=CH of 5-HMF ring [16]. Possible thermal decomposition products of sugar were shown in Fig. 2 [8]. In addition, compared with the other spectra, another new absorption band was detected at 1192 cm^{-1} in the cured adhesive that was attributed to dimethylene ether bridges [1], [9], [16]. These observations revealed that 5-HMF was produced by thermally decomposition of sugar at acidic pH, and chemical interaction occurred between CS - 5-HMF and MT - 5-HMF with dimethylene ether bridges. Possible reaction mechanisms between CS - 5-HMF and MT - 5-HMF were shown in Fig. 2. All observations showed that the crosslinked cured resin structure was obtained by the CS - CA

esterification reaction and chemical interactions between CS - 5-HMF and MT-5-HMF.

The curing mechanism of CS-MT-S-TA resin, which has a similar chemical structure, is given in Fig. 3.

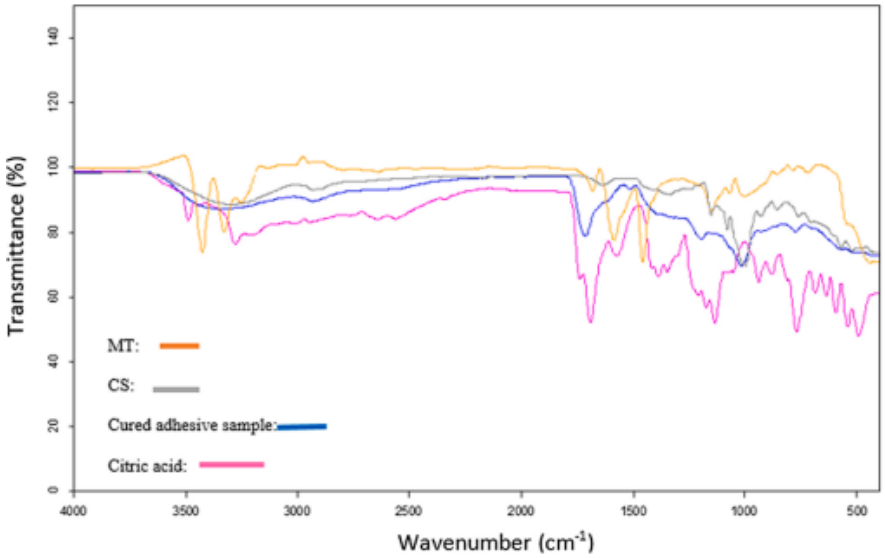

Fig. 1 FT-IR spectra of MT, CS, CA and cured adhesive sample

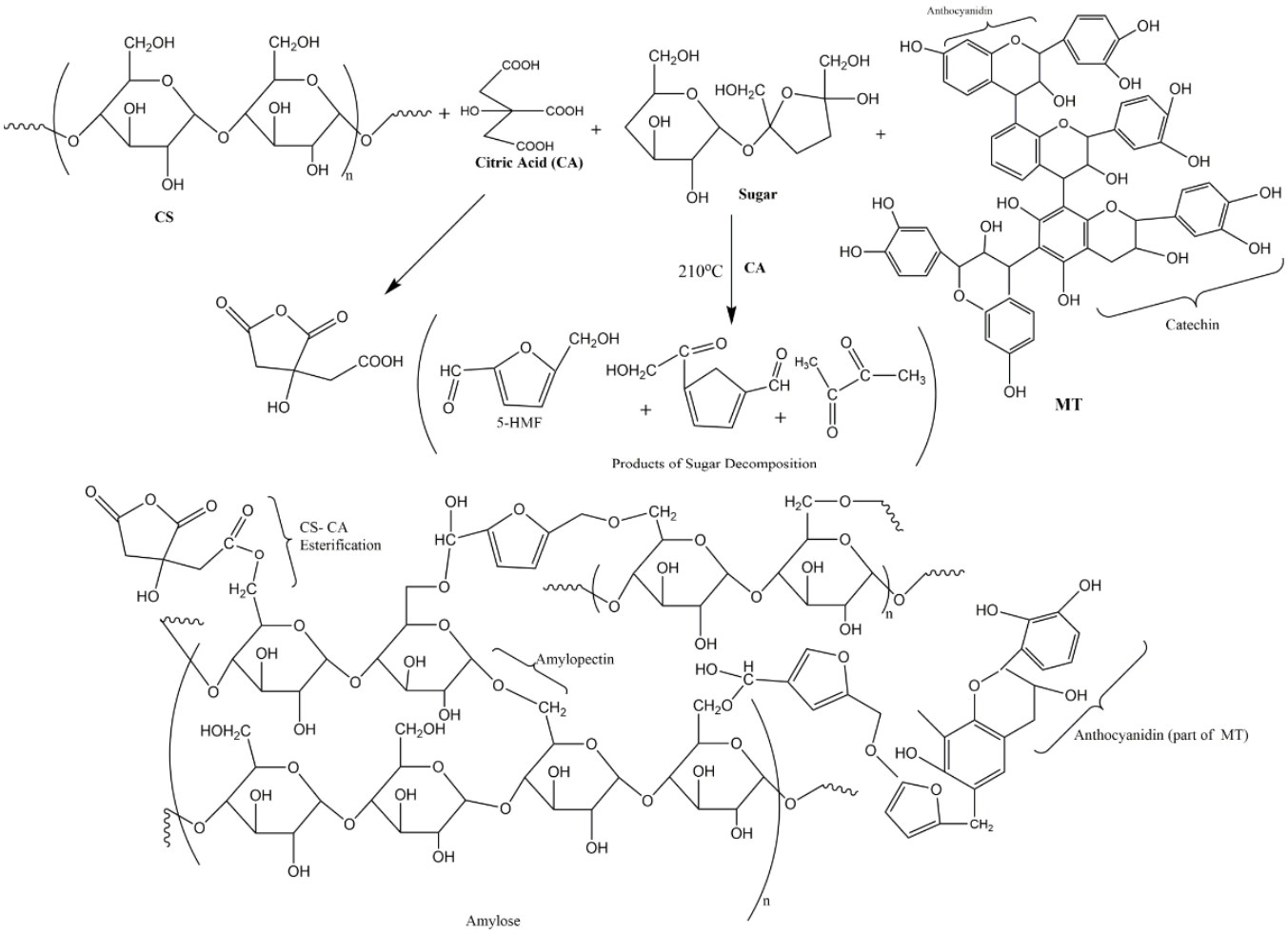

Fig. 2 The possible curing mechanism of CS-MT-S-CA resin

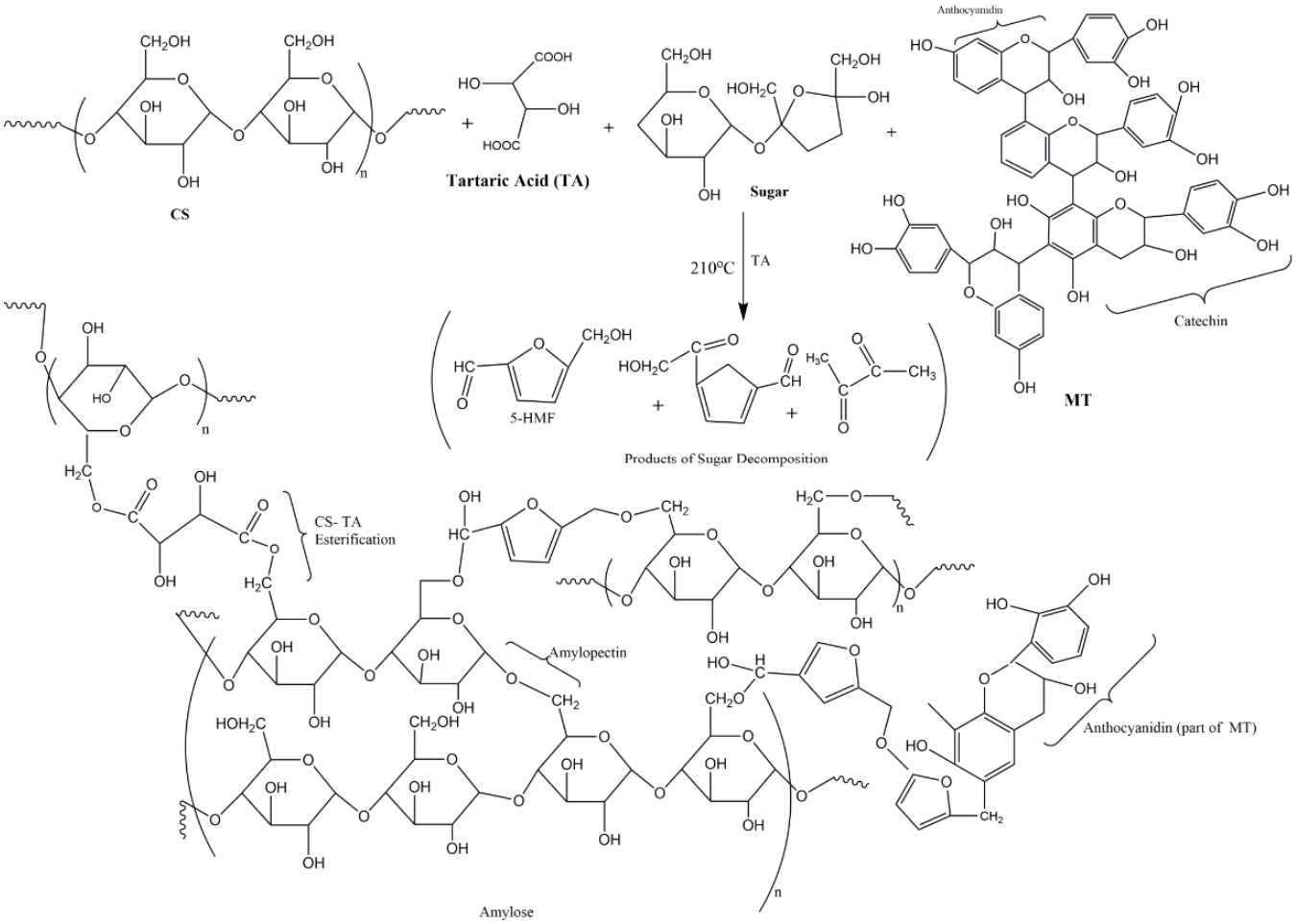

Fig. 3 The possible curing mechanism of CS-MT-S-TA resin

TABLE I
SUMMARY OF THE TEST RESULTS OF THE PARTICLEBOARDS

Wood Adhesive	Thickness (mm) Density (kg/m^3)	IB (MPa)	BS (MPa)	MOE (MPa)	Surface Soundness (MPa)
CS-MT-S-CA	10,64 750	0,90	14,83	3382,23	1,05
CS-MT-S-TA	10,56 691,54	0,63	10,22	2407,60	0,84
P2 EN312,2010 [c]		≥ 0,40	> 11	> 1800	> 0,80

b SD: standard deviation.
c EN: European standard target values for type P2, 6–13 mm.

D.Particleboard Preparation and Testing

In order to examine the performance of the developed resin formulation, laboratory-scale particleboards were produced and the physical (thickness and density) and the mechanical test results (IB, surface soundness, BS, and MOE) of the particleboards were illustrated in Table I. Since the boards were intended to be used in a dry environment, water uptake and thickness swelling tests were not performed. Boards bonded with the developed bio-based adhesive formulation exhibited promising mechanical and physical properties and generally satisfied the requirements of the standard for interior grade particleboards of the P2 class of EN 312. The results showed that the mechanical values of the boards were better when CA was used as a hardener.

E. Formaldehyde Content by Perforator Method

The formaldehyde content of the produced boards with the synthesized CS-MT-S-CA resin was measured as 1,28 ± 0,2 mg formaldehyde/100 g of particleboard and the formaldehyde content of the produced boards with the synthesized CS-MT-S-TA resin was measured as 1,50 mg formaldehyde/100 g of particleboard according to the European Norm (EN 12460-5) [1]. The measured emission values of produced particleboards are due to the formaldehyde generated just by wood, press parameters, and environmental factors and are not due to the adhesive [17]. It can be stated that a very low formaldehyde content has been obtained compared to formaldehyde-based resins [18].

IV. CONCLUSION

In conclusion, we synthesized a fully bio-based wood adhesive containing CS, MT, S, CA and CS, MT, S, TA. The cured adhesive chemical structure was proved that cross-linked adhesive networks were formed. Furthermore, to observe the performance of the prepared resin formulations, laboratory-scale particleboards were produced. Their physical, mechanical properties and formaldehyde content values were determined

[1]. All of the obtained test results revealed that the board's properties made with the synthesized bio-based resin generally met the requirements of panels for interior fittings used in dry medium (P2) according to European norms EN 312 (2010) [1]. In addition to the good mechanical test results of the board, it was observed that the panels produced with the developed bio-based resin formulation had a significantly lower formaldehyde content. As a result, it can be said that this study contributes to completely green, cost-effective, sustainable and formaldehyde-free wood adhesive studies for the production of internal grade particleboard.

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